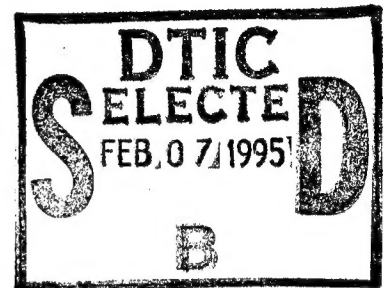


OFFICE OF NAVAL RESEARCH

GRANT or CONTRACT N00014-91-J-1045

R&T Code 4132047

FINAL REPORT



"Synthesis Morphology and Properties of Semicrystalline Block Copolymers"

by

Robert E. Cohen

Massachusetts Institute of Technology
Department of Chemical Engineering
Cambridge, MA 02139

January 10, 1995

19950203 134

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale; its distribution is unlimited.

REPORT DOCUMENTATION PAGE

OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 10 January 1995	3. REPORT TYPE AND DATES COVERED FINAL REPORT 9/9 - 9/94	
4. TITLE AND SUBTITLE "Synthesis, Morphology and Properties of Semicrystalline Block Copolymers"		5. FUNDING NUMBERS N00014-91-J-1045 4132047	
6. AUTHOR(S) Robert E. Cohen			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) M I T Department of Chemical Engineering Cambridge, MA 02139		8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) O N R 800 N. Quincy Street Arlington, VA 22217-5660		10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION/AVAILABILITY STATEMENT distribution unlimited		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Three years of research on the synthesis, structure and properties of semicrystalline block copolymers are summarized. Novel aspects of this relatively unexplored category of microphase-separated materials include: strongly path-dependent morphologies, unusual gas transport characteristics, compositionally enriched surfaces and favorable mechanical properties. Two industrial and one academic collaborations are mentioned. DTIC QUALITY INSPECTED 4			
14. SUBJECT TERMS Polymers: synthesis, structure, properties		15. NUMBER OF PAGES	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

Research Summary

While a great fraction of the research effort on block copolymers proceeds in the arena of heavily-studied amorphous/amorphous diblock copolymers, we launched a project to investigate the class of block copolymer polymers in which one of the block sequences had the capacity for crystallization. Beyond the simple fact that such a study would lead us to 'open territory,' we noted in advance that there were a few existing theoretical studies (1,2) to provide guidance for our experimental work and a very large audience of industrial researchers committed to the improvement of properties of commodity semicrystalline thermoplastics such as nylon and polyethylene.

Our approach, as in previous ONR-supported research in our laboratory, included a component of in-house synthesis of novel copolymers. The novel macromolecular species made by us were complemented by samples provided by Goodyear and DuPont. Some of our specially synthesized copolymers were sent to SUNY Buffalo for incorporation into a research program on polymer surfaces.

Detailed research results are summarized in the paragraphs which follow. Student and postdoctoral coworkers, publications and technology transition interactions are listed in separate sections later in this report.

Diblock copolymers of (ethylene-co-butylene)-b-(ethylethylene) (EBEE) were used to evaluate scaling laws describing the molecular weight dependence of the lamellar domain spacing of semicrystalline block copolymer systems. Small angle x-ray scattering was used to measure lamellar domain spacings for a series of EBEE samples. Experimental results were in good agreement with the predictions of the equilibrium theory of Whitmore and Noolandi (1). X-ray pole

- (1) M. D. Whitmore and T. Noolandi, *Macromolecules*, **21**, 1482 (1988).
- (2) E. A. DiMarzio, C. M. Guttman and J. D. Hoffman, *Macromolecules*, **13**, 1194 (1980).

By _____	
Distribution _____	
Availability _____	
Dist	Avail and/or Special
A-1	

figure analysis and small angle x-ray scattering were also used to determine the lattice unit cell orientation with respect to the lamellar microstructure. The x-ray data indicate that the orientation of the crystallized EB chains is perpendicular to the lamellar normals, unlike the chain folding which has been observed in semicrystalline homopolymers and proposed for semicrystalline diblock copolymers where the crystallized chains align roughly parallel to the lamellar normals. The unusual chain folding observed for EBEE is attributed to the influence of topological constraints in the EB blocks which crystallize within the amorphous lamellar microdomains present in the heterogeneous melt phase of the block copolymers.

A diblock copolymer containing polystyrene and linear polyethylene was also synthesized for our use by Dr. M. A. Drzewinski of EniChem using anionic-to-Ziegler/Natta transformation reaction. Combined evidence from 2-D small angle x-ray scattering and wide angle x-ray pole figure analysis showed conclusively that the polyethylene chains crystallize within the heterogeneous structure in a manner which leaves the polyethylene chains (c-axis) parallel to the lamellar surfaces.

A series of semicrystalline diblock copolymers of poly(ethylene)/poly(ethylene-propylene) (E/EP) were supplied to us by Dr. A. Halasa of Goodyear. These polymers were subjected to high levels of plane strain compression using a channel die. Deformations were imposed both below and above the melting point of the E block. The crystallographic and morphological textures were examined using wide-angle x-ray diffraction pole figure analysis and two dimensional small-angle x-ray scattering. The lattice unit cell orientation of the crystallized E chains with respect to the lamellar superstructure was determined, as well as the lamellar orientation relative to the specimen boundaries. When the copolymers are textured above the E block melting point at various compression ratios, the lamellae orient perpendicular to the plane of shear, while texturing below T_m causes the lamellae to orient parallel to the plane of shear. The orientation of the crystallized E chains was perpendicular to the lamella normal, irrespective of the texturing temperature. A set of triblock copolymers (E/EP/E) was also studied in a similar way. For these materials it was possible to obtain both perpendicular and parallel morphologies depending on the level of applied shear stress applied above to T_m .

The E/EP and E/EP/E copolymers were examined for their utility in gas separation applications. Gas permeability coefficients P for several gases (He, CO₂, CH₄, O₂, N₂) were measured at 25°C. A simple model successfully described the gas transport in these polymer systems. It predicts the permeability of a randomly oriented spherulitic diblock specimen from the permeabilities of the individual lamellar regions of the copolymer. Model predictions were in excellent agreement with the experimental data. The upper bound (lamellae aligned in parallel with respect to the permeation direction) and lower bound (series lamellar alignment) models were calculated and compared to a limited amount of corresponding experimental data on oriented specimens.

We also studied gas transport in a few novel diblock copolymers which contained only amorphous moieties. In one example, a selective solvent was used to develop a uniform microporous structure in a polystyrene-polymethylmethacrylate block copolymer. Pore diameters in the range of 100-500 Å were produced. Gas permeation measurements demonstrated a dramatic, five order of magnitude, increase in permeability coefficient associated with the throughgoing microporous structure. These high flux membranes retained some selectivity for certain gas pairs as expected for transport based on Knudsen diffusion in the porous materials. In a second example, the equilibrium solubility of gases in a star-branched SB block copolymer was reliably estimated from a volume fraction weighted average of the homopolymer solubilities; the value of heat of solution of gas in SB block copolymer was between the two values associated with the constituent homopolymers. Diffusion coefficients for gases in SB block copolymers were bracketed by the homopolymer values over the range of temperature employed, but the activation energies for diffusion in SB are higher than either of the homopolymer values. The anomalous temperature dependence and the inability of a computer simulation to reproduce experimental diffusion coefficient values for SB supported the concept of a temperature dependent restriction on chain mobility in the polybutadiene regions of the SB block copolymer. This β factor has values of about 2-3 at room temperature but decreases to unity when the polystyrene chains become mobile at the polystyrene T_g . The immobilization of the B chains cause a decrease in the rate of gas diffusion through the B region relative to homopolymer B, and this β factor showed a selectivity based on molecular diameter.

In a final piece of work on gas transport in block copolymer systems we studied diffusion solubility and permeability for He, CO₂, Ar and CH₄ in polybutadiene (PB) and in polybutadiene reacted in the solid state to various extents with aqueous bromine. Analysis of the sorption curves and x-ray emission spectra showed that the bromination created a heterogeneous membrane with an outer brominated skin and an unreacted core. At relatively low extent of bromination, the diffusion and permeability coefficients for CO₂, Ar and CH₄ became immeasurably small after about 3% bromination. The ideal separation factor for gas pairs with different molecular size increased with bromination, suggesting applications in gas separation processes.

Finally we were active in the study of mechanical behavior of our semicrystalline systems. One study focused on our efforts to obtain mechanically tough compositions based on the brittle semicrystalline homopolymer isotactic polystyrene. The approach included the anionic synthesis of isotactic polystyrene (iPS) and diblock copolymers of iPS and polybutadiene (PB) rubber. The diblocks were successful in emulsifying pools of rubber in blends of iPS and PB. A micromechanical toughness test was developed and used to demonstrate the dramatically enhanced toughness of the emulsified blends over the toughness of either the iPS homopolymer or of binary blends of iPS and PB. We also studied precipitated blends of two crystallizable polybutadiene (PB) isomers in terms of crystallization and phase behavior, morphology, and tensile mechanical properties. The isomers were syndiotactic 1,2 PB ($M_v=32.5k$ g/mol) and trans 1,4 PB ($M_v=425k$ g/mol). As predicted by Flory-Huggins theory, the blends exhibit heterogeneous behavior over the full range of composition. Degree of heterogeneity due to precipitation is on the order of 5μ or less, whereas spincast blends of amorphous (atactic 1,2 PB/mixed cis/trans 1,4 PB) homopolymers give macrodomains up to 50μ in diameter. Tensile properties of the crystalline blends are intermediate between those of the corresponding crystalline homopolymers, while tensile properties of the amorphous blends are generally worse than either of the amorphous homopolymers. But in both cases, property enhancement is evident at approximately 10% 1,2 PB content. Additionally, mechanical properties at break of the s-1,2 PB/trans 1,4 PB crystalline blends are improved by addition of 5-10% amorphous 1,2 PB/1,4 PB diblock copolymer. The effect of block molecular weight and micro-phase behavior on compatibilization of the crystalline homopolymers was also

investigated. Heterogeneous diblocks enhance blend properties to a greater extent than homogeneous diblocks. In blends with enhance properties, percent coverage of interfacial surface area by diblock is on the order of 10%.

List of Students and Postdocs

Moirá Marx Nir, Ph.D., 1991
Luigi A. Cazzaniga, Ph.D., 1991
David H. Rein, Ph.D., 1991
Peter Kofinas, Ph.D., 1994
Uchu Mukai, SM., 1992
Anuj Bellare, Postdoctoral Associate, 1993

List of Publications: Robert E. Cohen with co-authors indicated.

1. Spatial Organization of Polymer Chains in a Crystallizable Diblock Copolymer of Polyethylene and Polystyrene, *Macromolecules*, **27**, 2321 (1994) with A. Bellare and M.A. Drzewinski.
2. Surface Study of Diblock Copolymers of Polydimethylsiloxane and Nylon 6 by Electron Spectroscopy for Chemical Analysis, *Macromolecules*, **27**, 2206 (1994) with X. Chen and J. A. Gardella, Jr.
3. Selectivity and Permability of Microporous Block Copolymer Membranes, *Journal of Polymer Engineering*, **12**, 353 (1993) with D.H. Rein and R.F. Baddour.
4. Gas Permeability of E/EP Semicrystalline Diblock Copolymers, *Polymer*, **35**, 1229 (1994) with P. Kofinas and A. F. Halasa.

5. Toward a High-Impact Isotactic Polystyrene, *Polym. Eng. Sci.*, **34**, 1005 (1994) with L.A. Cazzaniga.
6. Blends of Crystallizable Polybutadiene Isomers, *Rubber Chem. Tech.*, **66**, 295 (1993) with M.M. Nir.
7. Solubility and Diffusion of Polybutadiene in Polystyrene at Elevated Temperatures, *Macromolecules*, **26**, 1287 (1993) with P. Nealey and A.S. Argon.
8. Chain Folding in EBEE Semicrystalline Diblock Copolymers, *Macromolecules*, **25**, 5030 (1992) with K. Douzinas.
9. Anionic Polymerization of Lactams in the Presence of Metal Dialkoxyaluminum Hydrides: Presentation of a New Mechanism, *Macromolecules*, **25**, 2004 (1992) with N. Mougín, C.A. Veith and Y. Gnanou.
10. Gas Solubility and Diffusion in a Polystyrene/Polybutadiene Block Copolymer, *J. Applied Polymer Sci.*, **45**, 1223 (1992) with D.H. Rein and R.F. Baddour.
11. Gas Transport in Polybutadiene Treated with Aqueous Bromine, *J. Polymer Sci., Polymer Physics*, **31**, 403 (1993) with D.H. Rein and R.F. Baddour.
12. Viscometry Constants for 1,4 Polybutadiene in Tetralin at 135°C, *J. Appl. Polymer Sci.*, **46**, 1503 (1992) with M.M. Nir.
13. Evaluation of Domain Spacing Scaling Laws for Semicrystalline Diblock Copolymers, *Macromolecules*, **24**, 4457 (1991) with K. Douzinas and A.F. Halasa.

14. Synthesis and Characterization of Isotactic Polystyrene/Polybutadiene Block Copolymers, *Macromolecules*, **24**, 5817 (1991), with L.A. Cazzaniga.
15. Gas Solubility in Glassy Polymers - A Correlation with Excess Enthalpy, *Polymer*, **33**, 1696 (1992) with D.H. Rein and R.F. Baddour.
16. Modification of Polystyrene/Polybutadiene Block Copolymer Films by Chemical Reaction with Bromine and Effect on Gas Permeability, *Macromolecules*, **24**, 3612 (1991) with J. Csernica, D.H. Rein, and R.F. Baddour.
17. Synthesis of Polydimethylsiloxane-Nylon 6 Diblock Copolymers, *Die Makromol Chemie*, **42/43**, 241 (1991) with C.A. Veith.
18. Mechanical Properties of Blends of Crystallizable Polybutadienes Containing Amorphous Polybutadiene Diblock Copolymers, *Rubber Chem. Tech.*, **67**, 342 (1994) with M. M. Nir.
19. Morphology of Highly Textured Polyethylene/Polyethylenepropylene Semicrystalline Diblock Copolymers, *Macromolecules*, **27**, 3002 (1994) with P. Kofinas
20. Melt Processing of Semicrystalline E/EP/E Triblock Copolymers Near the Order-Disorder Transition, *Macromolecules*, in press, with P. Kofinas.
21. Morphologies of Polydimethylsiloxane-Nylon 6 Diblock Copolymers and Blends, *Polymer*, **32**, 1545 (1991) with C.A. Veith and A.S. Argon.

Collaborations/interactions

Dr. Adel Halasa of Goodyear supplied us with several sets of crystallizable block copolymers. Based on our collaboration, two joint MIT/Goodyear publications were produced

(Numbers 13, 4). Lectures at Goodyear were given by R.E. Cohen on the morphological features of these materials (1993) and their gas transport properties (1991).

Dr. Michael Drzewinski of EniChem synthesized a special polystyrene/polyethylene which enabled us to verify some earlier work on chain organization in semicrystalline block copolymers. He is co-author of paper number 1 listed above.

Dr. Joseph Gardella of SUNY Buffalo was made aware of our novel nylon-polydimethylsiloxane block copolymers by Ken Wynne of ONR. Gardella was intrigued by their possibly interesting surface properties. Publication number 2 above documents this successful collaboration.

Highlights

Three significant publications:

The most significant publication is number (13) listed on page 6 of this report. This paper represents the first experimental verification of two existing theories of microphase separation in semicrystalline block copolymers. The counter-intuitive domain spacing scaling laws arising from these theories, i.e., the reduction in long period with increasing amorphous block length, showed through very clearly in the set of SAXS data we produced.

Along these same lines, paper number (8), page 6, is considered to be the second most significant in the list provided. Here we showed that chains align parallel to lamellar surfaces in the crystalline regions of semicrystalline block copolymers when the crystallization proceeds from a heterogeneous lamellar melt. Important consequences are likely in mechanical, dielectric and other physical properties. Controversial counter-examples appear in the literature.

Paper (11) on bromine-treated polybutadiene is potentially very significant from an applications perspective. We discovered that very modest levels of bromination produced a modified polybutadiene rubber which has gas barrier properties superior to those exhibited by butyl rubber. The latter material has at present an essential monopoly on the barrier elastomer market.

One presentation:

While numerous presentations of ONR sponsored research occurred over the 3-year funding period, the most exciting and synergistic was clearly a 1991 lecture on gas transport in heterogeneous block copolymers presented at Goodyear Research. Here I was speaking to an eager audience, on a topic of direct commercial interest and involving some (but not entirely) samples provided by their own chemists. The free flowing discussion and mutuality of interest made for a memorable event.

One award:

Based in part on my ONR-sponsored research, I was selected to co-chair an ACS Macromolecular Secretariat Symposium on Polymer Blends, held at the 1993 August ACS meeting in Chicago. The visibility from the symposium led directly to my selection in 1994 as co-editor for the Americas of the Journal of Polymer Engineering.